# Notes | Gaseous State | Unit 3 | Sessional Exam | B.Sc 1st Year | Chemistry (Major) | AMU | Physical Chemistry | ruhulamin.ml

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|---|---|
| Status | In progress |
| Content Type | Notes |
| Chapter | Gaseous State |
| Course | Graduation |
| Difficulty Level | Medium |
| Mistake type | |
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| | |
|---|---|
| Previous Year Questions | |
| Reference | (A Textbook of Physical Chemistry) K. L. Kapoor<br>Aligarh Muslim University Professor adichemistry.com<br>britannica.com chem.libretexts.org |
| Subject | Physical Chemistry |
| Topic | |

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# Postulates of kinetic theory of gases

> 📌 The kinetic theory of gases is based upon certain essential postulates (which are supposed to be applicable to an ideal gas).

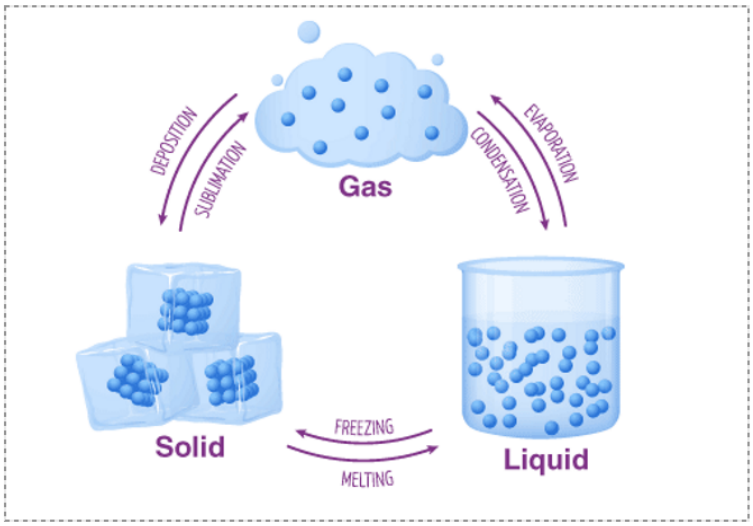
- Negligible gas particle's volume.
- No Force of attraction between particles.
- Particles moving Independently
- Random Motion of particles
- Collision between particles is perfectly elastic.
- No energy loss during collision.
- Laws of classical Mechanics are applicable.mainly: Second Law of Motion.
- Kinetic energy at an instant & for a given molecule: Energy from Large to very small possible.
- Average kinetic Energy = Constant (At a particular temperature)
  i.e KE is directly proportional to temperature.

# Deviation from ideal behaviour

Cause of deviation from ideal behavior of gas: Because of two important assumptions in Ideal gas:

- **Assuption**: Molecular Volume is negligible as compared to total volume of gas.
- **Reality**: Molecular volume is quite measurable and can not be ignored of gases
- **Assumption**: Gaseous Molecules have no force of attraction in between.
- **Reality** : Gaseous molecules have force of attraction between them.

## Evidence of Molecular volume of gas



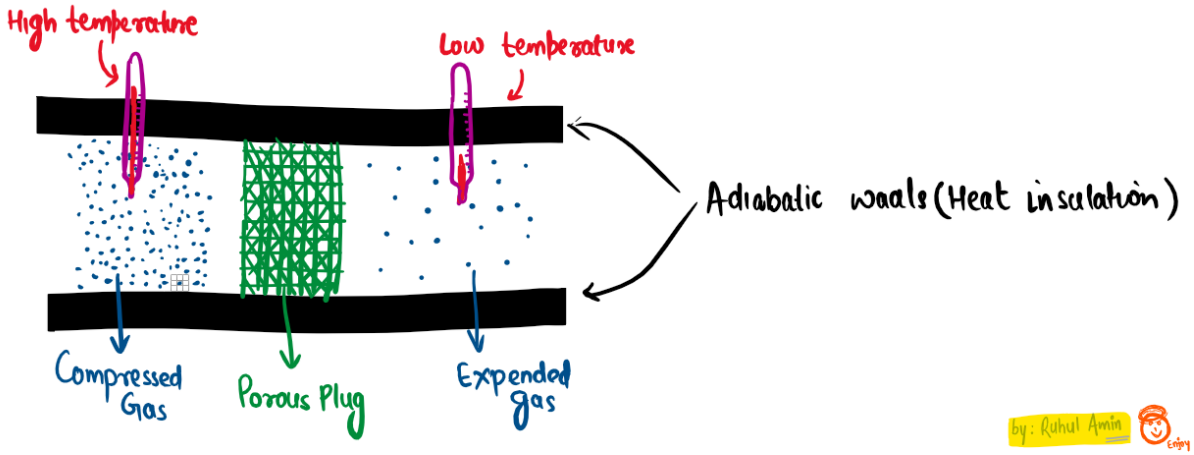

• Gases can be liquified and solidified in low temperature and High pressure.
• The gas liquified or solidified have some volume.
• This volume of gas is same irrespective of any state.
• liquified and solidified state of gases have force of attraction between molecule
• Solidified gases can be compressed up to certain extend only. Thus gases have appreciable volume, which is of same order as that occupies by same number of molecules in the solid state

## Evidence of Molecular Attration of gas:

• Gas molecules have vander waals force of attration,
Otherwise gas could never be liquified or solidified.
• On liquification and solidification, we only tend to reduce kinetic energy (by lowing temperature) and reduce distance b/ w molecules ( by high pressure).

> Joule-Thomson effect is also the evidence.

## Joule-Thomson effect




- When compressed gas is passed through porous plug in Adiabatic container the emerging gas is found to be cooler than entering gas
- This is because on expension, some work has to be done against the internal force of attraction, which require energy.
- This energy comes from the system itself.

# Van der Waals equation of state

- Van der Waals equation relates the relationship between the pressure, volume, temperature, and amount of Real gases.
- Furthermore more importantly, the Van der Waals equation is based on the molecular dimensions and molecular interactions with forces (attractive or repulsive forces).
- This is the modification of ideal gas law i.e **correction terms for pressure and volume** in ideal gas law.
- The equation is written as;

Expression for Van der Waals Equation for state :

Ideal Gas equation, $P_i V_i = nRT$

Real Gas equation, $\left(P + \frac{an^2}{V^2}\right)\left(V - nb\right) = nRT$

- Real Gas equation is known as Van der Waals Equation.

- The constants a and b have positive values and are characteristic of the individual gas.

# Critical Phenomena

- The concept of critical phenomena is associated with physical systems that undergo phase transitions at particular temperatures and or pressures.
- The phenomenon of a smooth merging of a gas into its liquid state under a **critical state** or critical point is referred to as ‘critical phenomenon’.
- At this stage, it is not possible to distinguish between the liquid and gaseous states of the substance as the two forms are existing in equilibrium.
- Three critical states or critical points are Critical temperature Tc,Critical pressure Pc and Critical volume Vc

## Definitions of Critical Constants

***Critical temperature*** $T_c$ is the maximum temperature at which a gas can be liquefied, i.e. the temperature above which a liquid cannot exist.

***Critical pressure*** $p_c$ is the minimum pressure required to cause liquefaction at the temperature $T_c$.

***Critical volume*** $V_c$ is the volume occupied by one mole of a gas at critical temperature $T_c$ and critical pressure $p_c$.

📌 For every gas, there is a limit of temperature above which it cannot be liquefied, no matter what the pressure is.

# PV isotherms of real gases

- Isotherm=**constant temperature**
- Isotherms are P-V curves that exist at a constant temperature.

- Isotherms refer to the different curves on the graph, which represent a gas state at different pressure and volume conditions but at constant temperature.
- PV= constant (Boyle's law)

It is the equation of **isotherm for ideal gases** where temperature is constant during the process

- At high temperatures,the isotherms look like those of an ideal gas.
- At low temperatures, the curves have altogether different appearances.
- let's understand PV Isotherms lie change of Pressure and volume at particular temperature in three different cases:

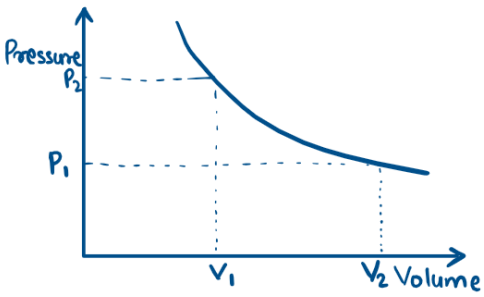
1. PV Isotherm at temperature  Above Critical Temperature
2. PV isotherm at critical temperature.
3. PV isotherm below critical temperature.

## PV isotherm of ideal gas

- Gases have volume inversely proportional pressure.
- The graph of P vs V in constant temperature is hyperbola.

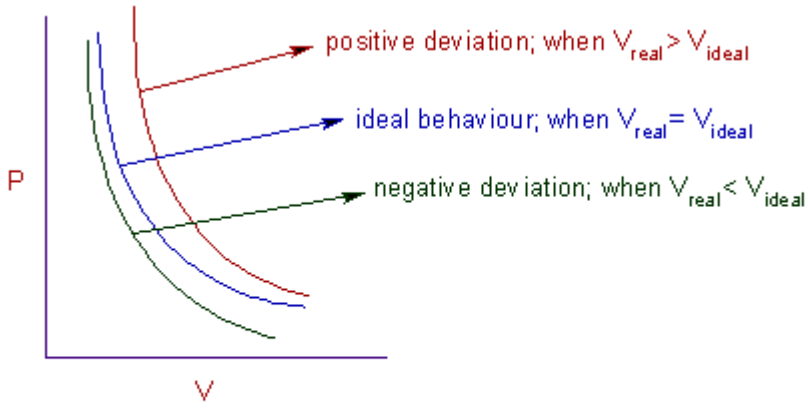
## PV Isotherm of real gas at temperature Above Critical Temperature

- Gases have volume inversely proportional pressure.
- As temperature is above critical temperature, gases donot change into liquid state. It just have gaseous state.
- This can be plotted in PV isotherm graph for high temperature as:




Temperature = Very high & Constant
At high volume ($V_2$), low pressure ($P_1$)
At low volume ($V_1$), high pressure ($P_2$)

- At temperature above critical temperature , Real gas behaves as ideal gas but donot trace it's exact trajectory. It means that the isotherms obtained by plotting pressure, P against volume, V for real gases do not coincide with that of ideal gas, as shown below.

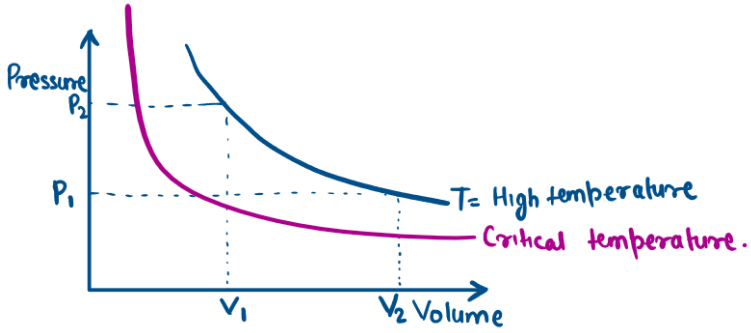



$V_{real}$= Volume of the real gas at given pressure.
$V_{ideal}$= Volume of the gas calculated by ideal gas equation at given pressure.

- It is clear from above graphs that the volume of real gas is more than or less than expected in certain cases. The deviation from ideal gas behaviour can also be expressed by **compressibility factor, Z.**
- The deviation from ideal gas of real gas due to molecular volume and force of attraction in real gases.

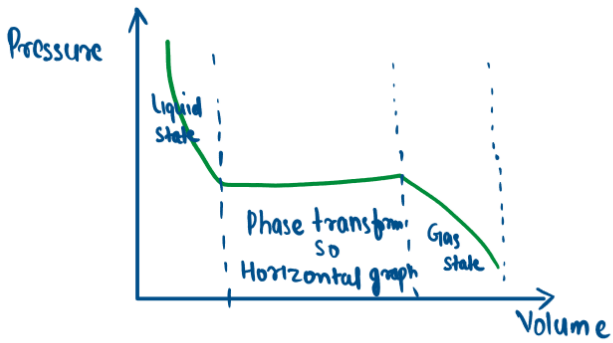
## PV Isotherm of real gas at Critical Temperature

- Pressure and volume is inversely proportional throught here also.
- At this stage of critical temperature, it is not possible to distinguish between the liquid and gaseous states of the substance as the two forms are existing in equilibrium.
- The PV isotherm at critical temperature is same as the PV isotherm of higher temperature, with just the difference in steepness of the graph. It's graph is more steeper.
- Graphically it can be described as:



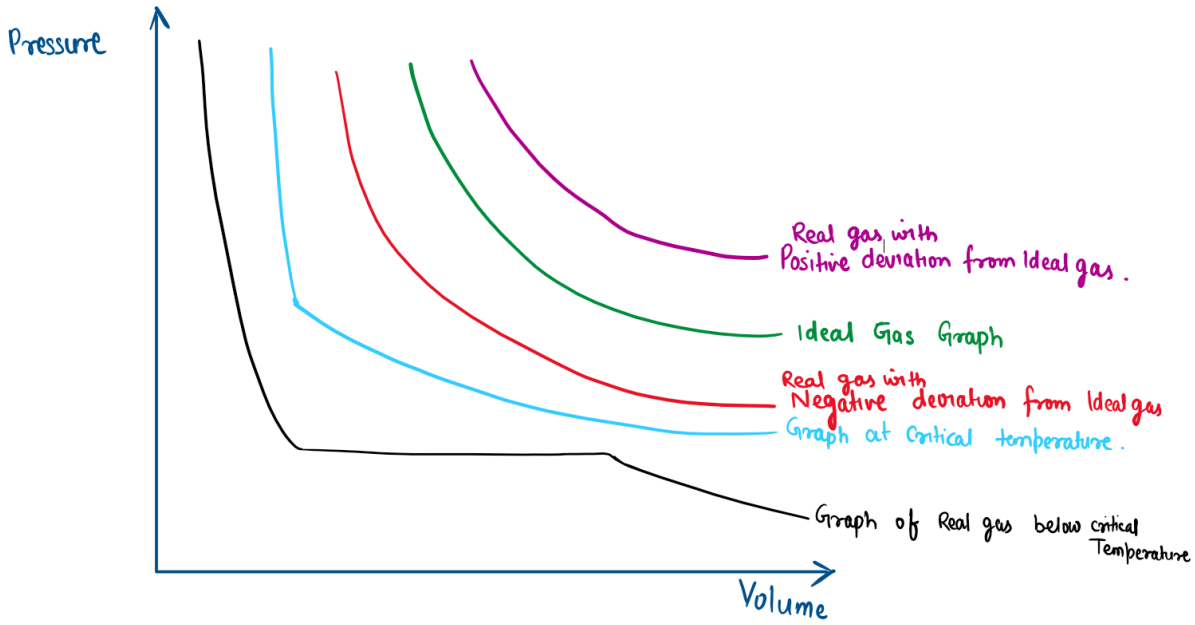

## PV isotherm of real gas below critical Temperature

- Below critical temperture, gases change it's phase from gas to liquid.
- During changing of phase from gas to liquid , energy is used up in phase transformation. So, even reducing volume, donot change the pressure.
- The energy are stored as bonds between particles and thus liquid state form from gas.
- When the gas is fully transform into liquid, further energy provided in the system shoots up the pressure .
- The pressure vs volume curve is not inversely proportional throughout. When phase transformation occurs,graph is horizontal , otherwise graph is inversely proportional.
- The graph can be shown as:




# Graph of PV Isotherm of real gas.

All the above three cases graph can be plot in one graph,as:


Pressure
Real gas with Positive deviation from Ideal gas.
Ideal Gas Graph
Real gas with Negative deviation from Ideal gas
Graph at Critical temperature.
Graph of Real gas below critical Temperature
Volume

# Continuity of State

- Continuity of State is the property of a transition between two states of matter, as between gas and liquid, during which there are no abrupt changes in physical properties.
- There is no difference between the liquid and the gas at the critical temperature.
- Continuity of State was observed by Andrew.
- There is no sharp transition between liquid and gaseous states in contrast to that observed on melting a solid.
- Gases and liquids are just the extreme stages of a fluid, with no fundamental distinction between the two. For this reason, an arbitrary decision has been made for the present discussion to define what is meant by the gaseous state. The definition will be based on the number **density.**
- When gas or liquid (under enough pressure) are heated up above critical temperature, they become gas-like or liquid-like **supercritical fluids,** than can gradually become each other with changing pressure, without phase change or phase boundary. It is like going along the slope instead of making a step.
- There is a unique point for every fluid, called the **critical point.** It is described by a critical temperature, a critical volume, and a critical pressure, at which **liquid and vapour become identical.**

😕 Confuse between Continuity of State and critical  points?

# Isotherm of Van der Waals Equation

- **Isotherms** refer to the different curves on the graph, which represent a gas state at different pressure and volume conditions but at constant temperature.
- Isotherm of Van der walls quation can be depicted as :

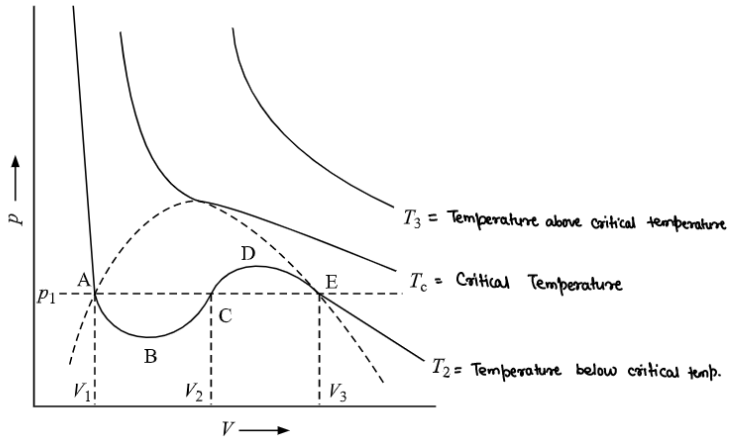
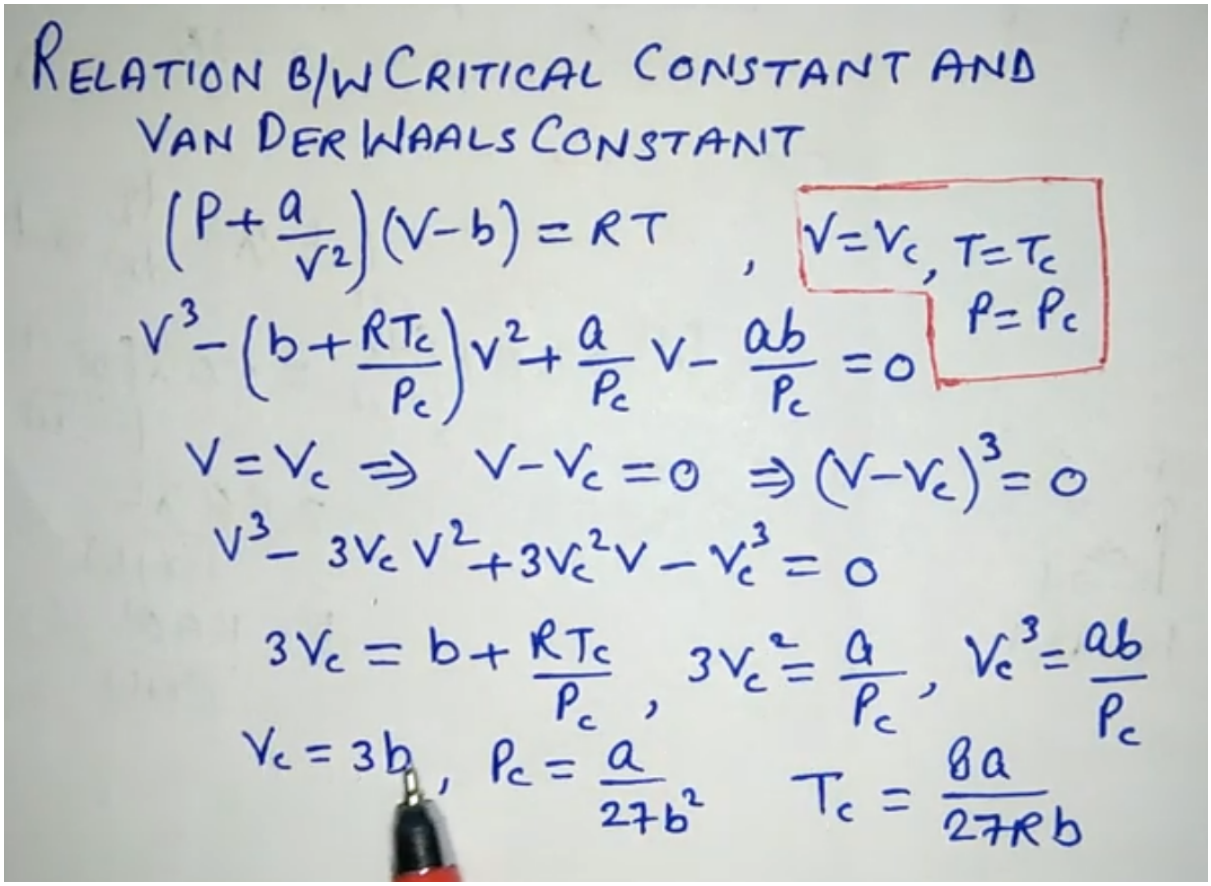



**Fig. . Van der Waals isotherms**

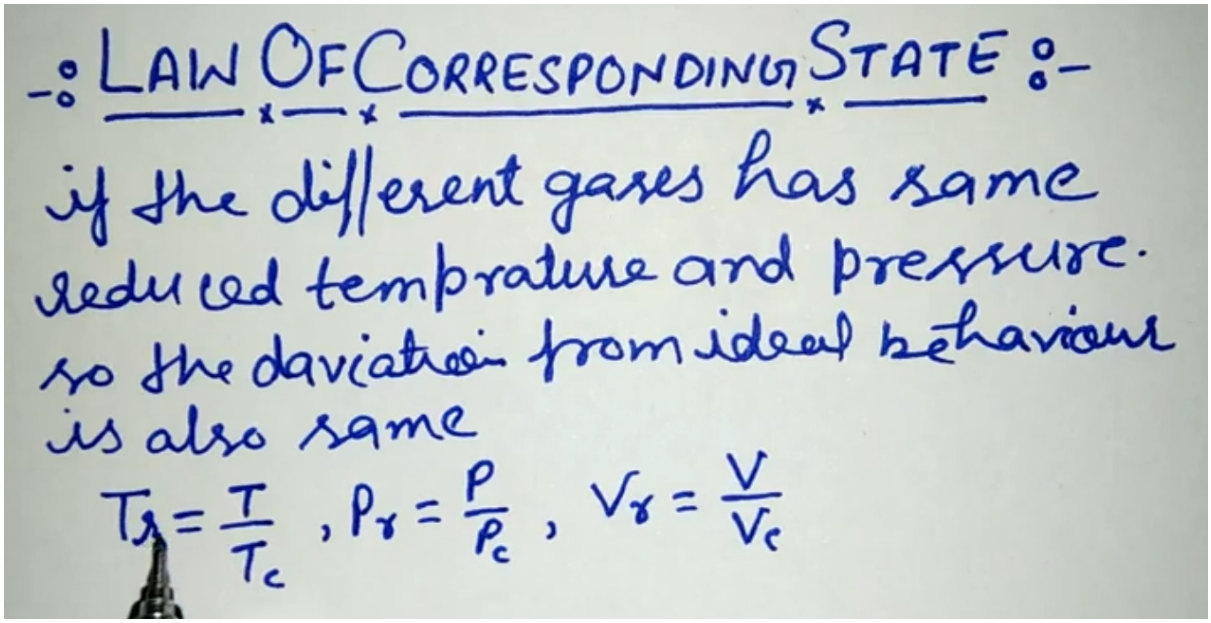
- Main Characteristics of van der waals isotherms are:
- :At higher temperatures such as T3 and in the higher volume region, the isotherms look much like the isotherms for a real gas.
- At a temperature lower than Tc the isotherm exhibits a maximum and a minimum.For certain values of pressure, the equation gives three roots of volume, e.g., V1 , V2 and V3 at pressure p1 .
- The sections AB and ED of the van der Waals curve at T2 can be realized experimentally. ED represents **supersaturated** (or **supercooled**) vapour and AB represents **superheated** liquid. Both these states are metastable. These are realized only when the volume is changed very slowly. These states are unstable in the sense that slight disturbances are sufficient to cause the system to revert spontaneously into the stable state with the two phases present in equilibrium.
- The section BCD of the van der Waals isotherm cannot be realized experimentally. In this region the slope of the p–V curve is positive. Increasing (decreasing) the volume of such a system would increase (decrease) the pressure. The line BCD also represents the system in the metastable state.

- At the end points of the horizontal line AE, the conversion of gas into liquid or vice versa has just commenced, the system will have the same value of Gibbs function at the points A and E.

# Relationship between critical constant and van der waals constants

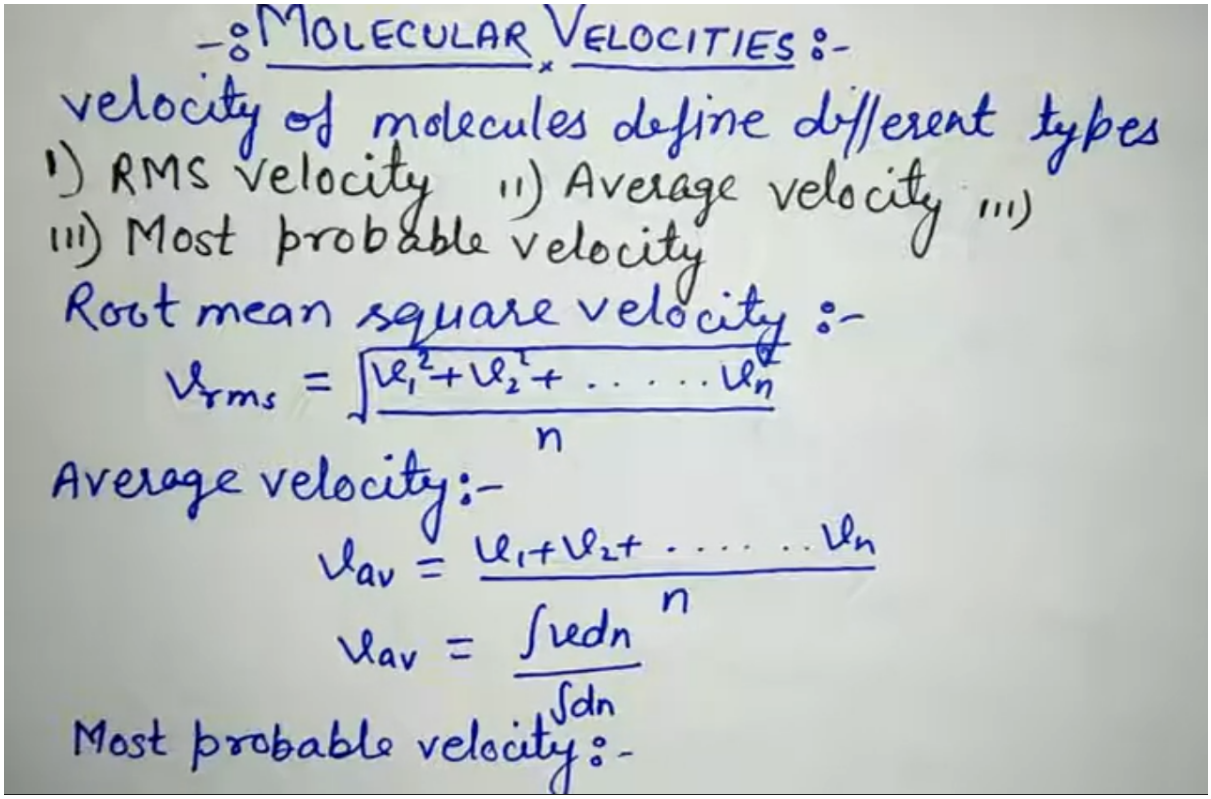



# The law of corresponding states


:- LAW OF CORRESPONDING STATE :-
if the different gases has same reduced temprature and pressure. so the daviation from ideal behaviour is also same
$T_r = \frac{T}{T_c}$ , $P_r = \frac{P}{P_c}$ , $V_r = \frac{V}{V_c}$

## Reduced Equation of state

## Molecular velocities:


-:MOLECULAR VELOCITIES:-
velocity of molecules define different types
I) RMS velocity II) Average velocity III)
III) Most probable velocity
Root mean square velocity :-
$v_{rms} = \sqrt{\frac{v_1^2+v_2^2+\ldots\ldots v_n^2}{n}}$
Average velocity:-
$v_{av} = \frac{v_1+v_2+\ldots\ldots v_n}{n}$
$v_{av} = \frac{\int v dn}{\int dn}$
Most probable velocity:-

**Root Mean Square velocit**

**Average Velocity**

**Most probable velocity**

## Qualitative discussion of the Maxwell's distribution of Molecular velocities

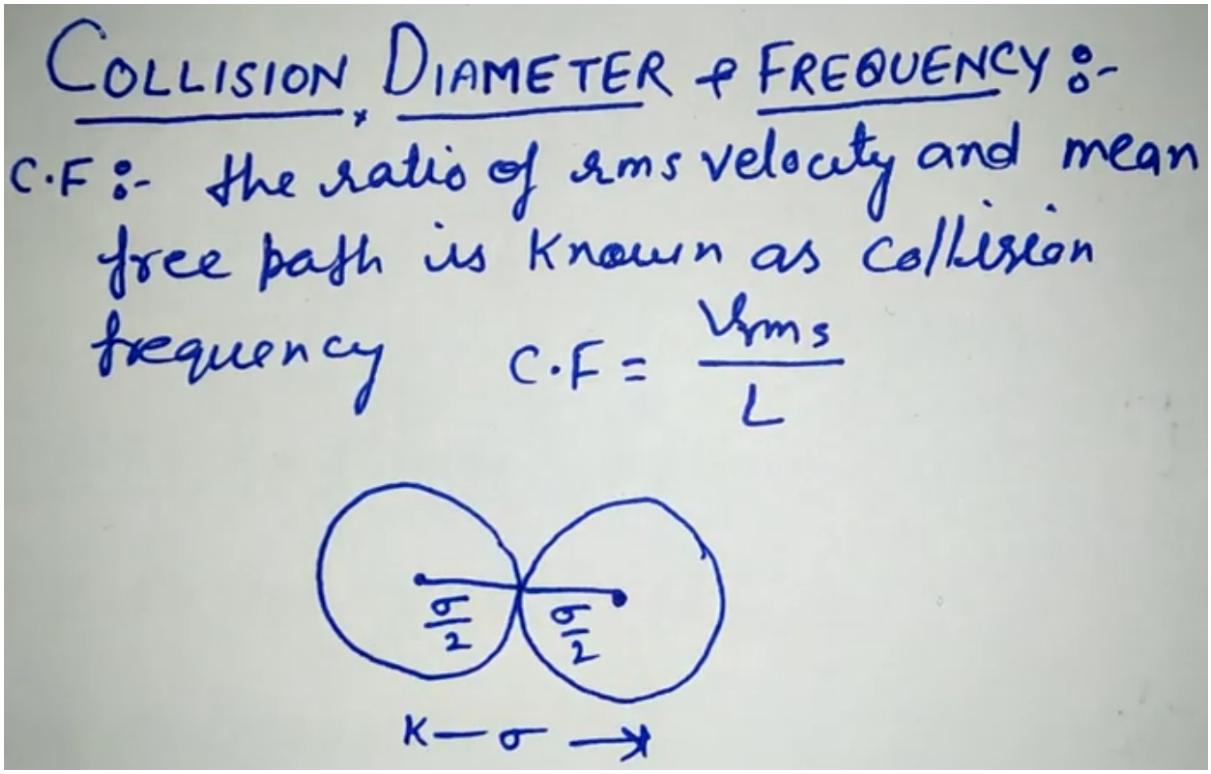
## Collision number

# Mean free path

- Distance covered by a molecule between two consequetive collision is called **free path**.
- Average of all free path is mean free path.
- Mean free path depends on fluid property like viscosity , pressure, and density.

# Collision frequency and Collision diameter

- Collision per second is Collision frequency


COLLISION, DIAMETER & FREQUENCY :-
C.F :- the ratio of rms velocity and mean free path is known as collision frequency
C.F = Vrms / L
σ/2
σ/2
K — σ →

- Distance between the centre of two particle colliding is known as collision diameter.

# Liquification of gases( Based on Joule thomson effect)

- Joule thomson effect occur below a particular temperature known as inversion temperature.

Some more References:


1. **M Malaz :** Master in Physics
2. **qsstudy.com/continuity-of-state/**
3. chemistry.stackexchange.com
4. https://www.youtube.com/@rqphysics1739